

current, giving decrease of the quotient A/K ; while base favours the A current and disfavours the K current. In other words, the anodic or acidic polarisation is favoured by base, disfavoured by acid; the cathodic or basic polarisation is favoured by acid, disfavoured by base. Anæsthetics (CO_2 ; Et_2O ; CHCl_3) act like acids and like rise of temperature, causing, at certain strengths, a greater relative diminution of A than of K, and therefore a diminution of the quotient A/K —temporary in the case of CO_2 and Et_2O , permanent in the case of CHCl_3 . In the weakest dilution that will produce any effect at all there may be increase of A, no increase, or a relatively smaller increase, of K, and therefore increase of the quotient A/K . These effects are, however, at present under examination, and will form the subject of a future communication. The tabular summary (p. 391) will at this juncture be sufficient to enable a comparison to be made between the effects of heat and cold and those of acids and alkalies.]

“On the Occurrence of Gallium in the Clay-ironstone of the Cleveland District of Yorkshire: Determination of Gallium in Blast-furnace Iron from Middlesbrough.” By W. N. HARTLEY, F.R.S., Professor of Chemistry, and HUGH RAMAGE, A.R.C.Sc.I., F.I.C., Assistant Chemist, Royal College of Science, Dublin. Received December 2,—Read December 17, 1896.

In the month of April of this year, we had the honour to submit to the Royal Society* a preliminary notice of the evidence we had obtained of the existence of gallium in the Yorkshire ironstone smelted at Middlesbrough-on-Tees.

We propose now to give a concise but detailed account of the methods of analysis carried out on the metal and the ore, and the determination of the quantity of gallium present.

Examination of the Blast Furnace Metal.

Method of Analysis.—The very large proportion of iron rendered the application of some special method of analysis necessary for the separation of metals present in minute proportions, and for the qualitative and quantitative examinations of the separated substances. We have successfully employed fractional precipitations and the spectrographic analysis of the precipitates, supplemented by gravimetric determinations of the purified gallium sesquioxide.

The sample of metal first received consisted of two small ingots, each weighing about 230 grams; small pieces, broken with difficulty

* ‘Roy. Soc. Proc.’ vol. 60, p. 35, 1896.

from these and heated in the oxyhydrogen flame, gave the gallium line $\lambda 4171.6$. The ingots were exceedingly hard, and practically resisted all attempts to reduce them to small pieces. One ingot, weighing 210 grams, was boiled with hydrochloric acid, until its solvent action on the metal had nearly ceased, when the liquid was decanted, and fresh acid poured on. The process was very slow, and, after 80 grams had been dissolved, the remaining piece of metal was scraped, to remove an adhering layer of carbonaceous matter, and the analysis of the products proceeded with. The liquid was filtered, and the black residue *A* washed. The filtrate was evaporated, to expel the excess of hydrochloric acid, water was added, and the solution, not being clear, was filtered. The residue *B* thus obtained had, when dry, a dark greyish colour. *Residues A and B.*

In the clear filtrate two rods of zinc were immersed, and during a period of one hour and three-quarters hydrogen was evolved, and metals were deposited on the zinc. The deposit was scraped off, and separated from the liquid by filtration. *Metallic deposit C.* To the filtered solution were added about 4 c.c. of lead acetate solution, and two rods of zinc were placed in the liquid, according to the method of Lecocq de Boisbandran,* by which, as the lead is precipitated, traces of other metals, such as copper, silver, indium, thallium, &c., are collected by the lead. *Metallic precipitate F.*

Fractional Precipitation by Ammonium Acetate.—The filtrate, in volume about 2 litres, was boiled, but as no precipitate formed, 15 c.c. or thereabouts of a solution of ammonium acetate were slowly added, and the solution boiled; the iron, being in the ferrous state, was retained in solution, whilst it was expected that the gallium would be precipitated as phosphate. After boiling for about twenty minutes, the substances precipitated were collected on a filter and washed. *Residue D.*

The filtrate was again boiled with about 10 c.c. of ammonium acetate, and the precipitate collected on a filter. *Residue E.*

Further Precipitation of Basic Acetates.—The filtrate from *E* was again boiled with ammonium acetate, the resulting precipitate being filtered off. It was much darker in colour than those previously obtained. *Sesquioxide metals G.*

The filtrate was evaporated until it became a saturated solution of ferrous chloride. It was allowed to cool and crystallise, and the operation was repeated upon the mother liquor. The two crops of crystals were mixed with others, which were obtained as follows. The solution from the remaining portion of the 210 grams of metal was filtered, and the filtrate evaporated. It was then allowed to cool and crystallise. The mother liquor was concentrated, and again allowed to cool and crystallise, the different crops of crystals

* 'Spectres Lumineux.'

being collected. The mother liquor from the last crop of crystals was evaporated almost to dryness to expel acid, and, after addition of water, rods of zinc were immersed in the solution, which was then left undisturbed for forty-eight hours. The zinc was found to have been almost all dissolved. The precipitated metals and the residue of zinc were washed and dried. *Residue H.* The filtrate, after three precipitations with ammonium acetate, was mixed with the mother liquor of the ferrous chloride crystals from the first portion, so that the liquid then represented the whole of the ingot. It was diluted, mixed with an excess of ammonia and ammonium sulphide, to precipitate all the iron and metals of that group still in the solution, and filtered. The filtrate was evaporated to dryness and gently ignited to expel ammonium salts. A residue was left, which contained the alkaline earths and alkaline metals.

The Spectrographic Analysis of the Residues and of the Precipitates.

From the foregoing description it will be observed that by partial solution the metals precipitable by iron may be looked for along with carbon, and, probably, some phosphides of iron and other metals. Such phosphides yield the flame spectra of the metals only, and not of the phosphorus combined with them. Precipitation with zinc in an acid solution was expected to give a deposit (*F* and *H*) which would yield the spectra of copper, silver, bismuth, lead, thallium, and tin in the oxyhydrogen flame, if these metals were not already precipitated by the iron, and present in the residues *A* and *B*; while *D*, *E*, and *G* are compounds which fall under the category of sesquioxide metals, including beryllium, aluminium, indium, gallium, and chromium. Of these, aluminium and beryllium were expected to show no spectra in the oxyhydrogen flame, and for these it was intended to use spark spectra.

The residue A, when dried in the water oven and gently heated, gave off fumes which indicated that an oil was present, and extraction with ether and subsequent evaporation did, indeed, yield a quantity of a brown oil.

The oxyhydrogen flame spectra of the substances separated were photographed, and the following are particulars regarding their spectra.

The insoluble residue A contained iron, manganese, copper, gallium, sodium, chromium, silver, and nickel.

The lines which served to identify the metals had the following wave-lengths:—

Iron	4208·0	4046·0	3929·8	3922·0	3904·8
	3898·5	3886·5	3860·0	3857·0	3841·0
	3834·0	3826·0	3824·5	3758·4	

and all the strong lines in the groups extending to 3441, corresponding to the solar line O.

Manganese .	4033·0	4032·0	4030·0	—	—	—
Copper.....	3290·0	3262·5	—	—	—	—
Gallium....	4171·6	4032·7	—	—	—	—
Sodium	5893·0	5688·0	4668·0	3303·0	—	—
Chromium..	4289·0	4274·0	4253·0	3606·0	3593·0	3578·0
Silver.....	3383·5	3282·1	—	—	—	—
Nickel	3525·0	3415·0	—	—	—	—

The insoluble residue B contained iron, copper, sodium, and a trace of potassium.

Iron.....	Groups of lines lying between 4045·0 and 3440·0					
Copper...	Lines with wave-lengths	3290·0	„	3262·5		
Sodium...	„	„	5893·0	„	3303·0
Potassium	„	„	4047·1	„	4043·5

The metals precipitated by zinc, C. These were iron, copper, silver, a trace of lead, also some sodium and potassium. There was also a trace of chromium, and this, like the trace of iron, was probably precipitated as basic chloride or as hydroxide. The wave-lengths of the lines of iron, silver, and copper need not be recapitulated.

Lead	4057	3682 and 3639
Chromium.....	4289	4274 „ 4253

The metals precipitated by zinc after addition of lead acetate, F.—The metallic deposit yielded a complex spectrum containing the lines already mentioned of the following elements: iron, chromium, copper, silver, gallium (*a trace*), potassium, sodium, and, of course, lead, as this had been added.

The lead here appears as a banded spectrum, the edges of the bands seen being those at wave-lengths:—

5675	5460	4980	4824	4657
4597	4370	4314	4225	4140
4061	4057	3985 and 3954		
Nickel lines....	3525	„	3415	

The copper lines were very strong, the silver weak.

The potassium lines were the following:—

	4047·1	4043·5 strong,
then much fainter—	3447·5	and 3446·5.

The precipitates of Phosphates and basic acetates D, E, and G.

Precipitate E.

Chromium	5206	4289·0	4274·0	4253·0
	3606	3594·0	3579·0	
Gallium.....	strong	4171·6 and	4032·7	
		(the latter somewhat weaker).		
Calcium.....	weak	4226·8		
Potassium.....	strong	4047·0	4043·5	
Sodium	strong	5893·0, faint	5685, and	3303·0

Precipitate D.

The chromium line 5206 did not appear in the spectrum of this precipitate. Both the gallium lines were very distinct, 4171·6 and 4032·7.

It is remarkable how very generally the spectrum of potassium appears along with that of the precipitated substances, whether metals or basic acetates.

Precipitate of basic acetates, G.

This contained iron, chromium, lead, gallium, potassium, and sodium. The lines were those which have already been particularised.

The Residue left by Zinc, H.—This was heated with aqua regia, when all but a very small quantity of silica with a trace of a metallic oxide dissolved. The liquid was filtered and the filtrate evaporated with excess of hydrochloric acid to remove nitric acid. It was diluted with water, when it showed a green colour.

It was saturated with sulphuretted hydrogen and filtered to separate the precipitate. The precipitate was partially soluble in sodium hydrogen sulphide, yielding a sherry-coloured solution; the constituent causing this colour was not identified, the quantity present being very small. The residue, insoluble in alkaline sulphide, contained copper and a trace of lead, but no mercury, bismuth, or cadmium.

The filtrate from zinc and precipitated metals I, was diluted and heated to boiling. It gave a precipitate, and therefore ammonium acetate was added to the hot liquid, and after boiling for several minutes it was filtered. The filtrate became turbid immediately; it was then boiled and more ammonium acetate added and then filtered; the filtrate again became turbid.

This precipitate was filtered off and heated in the oxyhydrogen flame.

It contained no gallium, but the spectrum gave lines of iron, copper, sodium, potassium, and a trace of lead.

It is evident that all the gallium was extracted by the repeated additions of ammonium acetate solution and boiling.

The various precipitates of basic acetates were mixed, with the exception of that from *I*, which contained no gallium. In order to separate phosphoric acid, the precipitates were fused with about three times their weight of mixed carbonates. Some potassium nitrate was added towards the end of the fusion, to convert chromium into chromates. The heavy metals were left as oxides or carbonates, the phosphoric acid going into solution. After extraction with hot water, the solution was filtered.

Filtrate L.

Coloured greenish by manganates, boiled with a few drops of alcohol to separate manganese as hydroxide. Solution, after again filtering from manganese, was yellow from chromates.

Residue M.

Dried and fused in a silver dish with caustic soda to dissolve gallium hydroxide. Extracted with water and filtered. *Residue* not examined further. *Solution* : acidified with HCl and ammonium chloride and ammonia added. The precipitate was filtered off, dissolved in HCl, and sparked to observe its spectrum.

These gallium spectra showed that there were still traces of chromium in the gallium chloride, and from this the gallium was purified completely by precipitation in a strongly acid solution with potassium ferrocyanide and subsequent removal of the iron by treatment with sodium hydrate, according to the method of Lecocq de Boisbaudran.*

The foregoing description of the analytical details proves the presence of gallium in the metal, and gives a clear indication of how it may be separated by a simple process.

In subsequent operations on the blast-furnace metal, the ferrous chloride was mixed with calcium carbonate, and the gallium was found to be all precipitated and capable of easy separation from the calcium salt.† Latterly it was found to be more convenient to boil the acid solution containing gallium with an excess of the iron under examination, and thus the gallium is concentrated in the residue which remains undissolved.‡

It became necessary to consider what was the source of the gallium contained in the iron. Was the gallium concentrated in the metal? Or did it pass into the slag of the converter? Was it originally contained in the ore, the lime, or the fuel? Was it easily volatilised, so as to pass off with fume or with flue dust?

* 'Comptes Rendus,' vol. 94, p. 1228.

† *Loc. cit.*, p. 1629.

‡ 'Comptes Rendus,' vol. 49, p. 1625.

On February 10th we received from Mr. C. R. Ridsdale, the Chemist at the North Eastern Co.'s Steel Works, at Middlesbrough, samples of the following materials:—

1. "Mixer metal," *i.e.*, mixed blast-furnace metal.
2. Roasted Cleveland iron ore.
3. Flue dust.
4. Tap cinder.
5. Manganese ore.
6. Lime.

On February 12th, photographs of the oxyhydrogen flame spectra of these substances were obtained.

The following are the particulars of this examination:—

1. The roasted Cleveland ore contained iron, sodium, potassium, manganese, chromium, nickel, copper, gallium, lead, and calcium.
2. The blast-furnace metal contained iron, sodium, potassium, manganese, nickel, copper, gallium, and lead.
3. Flue dust contained iron, sodium, potassium, manganese, chromium, nickel, copper, silver, gallium (doubtful), lead (strong), calcium, and rubidium. Rubidium was identified by the lines 4202 and 4216. (Thalèn.) Calcium by line 4226, in the blue.

It is evident now that gallium is contained in the ore and is concentrated in the metal.

1. The manganese ore (a 15 per cent. Spanish ore) contained iron, sodium, potassium, manganese, copper, silver, lead, indium, and calcium. The lines by which the indium and the silver were identified are as follows:—

Indium	4510·2	4101·3
Silver	3383·5	3282·1

The occurrence of indium is remarkable, as hitherto it has been found only in zinc blendes.

2. Tap cinder contained iron, sodium, potassium, manganese, copper, and lead.
3. Lime contained calcium, magnesium, potassium, and sodium, a trace of iron, and a trace of manganese.

The lime showed the following bands, characteristic of lime* :—

Band in the orange from 6253 to 6116, degraded towards the more refrangible side.

Band from 6075 to about 5900.

* 'Phil. Trans.,' vol. 185, p. 182.

Very strong band from 5598 to 5485.

Band of continuous rays with other bands discernible in it.

Less refrangible edge of band 5445.

Band in the same at 5422, 5390, 5359, 5341, 5322.

The more refrangible edge of band 5304.

Very narrow band in the blue, more like a very strong broad line from 4222 to 4215.

The magnesium oxide was identified by three bands, more or less connected by diffused rays.

1st. From 3929 to 3856

2nd. „ 3834 „ 3805

3rd. „ 3805 „ 3682

On these bands were seen ten iron lines, six in the first principal group and four in the second, all very faint, but with apparently the following wave-lengths, which correspond with the lines seen in oxyhydrogen flame spectrum of ferric oxide. They are also closely in approximation to, and probably identical with, the following arc lines, measured by Kayser and Runge in iron.

3860.03	3856.49	3826.04	3824.58
3758.36	3748.39	3745.67	3737.27
3735.0	3722.69	3720.07	

Roasted Cleveland Iron Ore. Process for the Extraction of Gallium.

This ore is a complex substance, and contains elements which render the complete extraction of the gallium very difficult. It is in great part soluble in strong hydrochloric acid, but the iron goes into solutions as a ferric salt, and difficulties arise in attempting to reduce it to the ferrous state. Zinc and iron are both liable to contain gallium, and, without a very careful examination of a quantity of the metal, it would be wrong to use them as reducing agents, seeing that the quantity of metal required in the process is large in comparison with the sample treated. Sulphurous acid and kindred substances yield sulphates which cause a quantity of the alkaline earths to separate as sulphates, and, as these precipitate in faintly acid solutions, there is a risk of basic gallium sulphate being carried down with them.

Dilute hydrochloric acid yields a solution poor in iron, but the dissolved matter is richer in gallium than the original ore. A large proportion of silicic acid is, however, contained in the solution.

Experiments were made on quantities of 50 grams of the ore, and the spectra from the sesquioxide metals were carefully compared with the spectra from the similar products from the metal, and we find that, as in the comparison of the original samples of ore and

metal, the gallium lines are decidedly stronger in the spectra of the substances extracted from the metal.

One kilo. of finely powdered ore was mixed with dilute hydrochloric acid of double normal strength, measuring about 1250 c.c. Some carbon dioxide was disengaged and an insoluble residue left which was removed by filtration. The filtrate was then heated when a gelatinous separation of silica occurred. After evaporation to dryness, a further addition of hydrochloric acid yielded a solution which was not highly coloured, and, presumably, did not contain much iron. The silica rendered insoluble was removed by filtration, and to the filtrate ammonium chloride and ammonia were added. The precipitate thus formed was dissolved in hydrochloric acid, reduced with sulphur dioxide, nearly neutralised, and boiled with sodium thiosulphate. The precipitate was dissolved in hydrochloric acid and again precipitated by ammonia.

This precipitate was examined for gallium. The insoluble residue was also examined, and a comparison of the two spectra showed that a larger quantity of gallium remained in the insoluble residue than was extracted by the acid. It was found that gallium could be extracted from this by fusion with caustic soda and lixiviation with water, and that the residue, after such treatment, contained no gallium. Operations on this particular ore were suspended until other samples had been examined.

The following ores from the collection in the Royal College of Science, Dublin, were examined:—

1. Yorkshire clay ironstone from near Middlesbrough.
2. Clay ironstone from Grosmont, Whitby, Yorkshire.
3. Northamptonshire ore (clay ironstone).
4. Black band ore, Mount Melville mine, St. Andrews.

One kilo. of each was reduced to fine powder, and 100 grams of Nos. 1, 2, and 3, and 500 grams of No. 4 were extracted with dilute hydrochloric acid as in the previous case. In each sample gallium was found, but the proportion was very small in the Northamptonshire ore, and still more minute in the black band. Without operating on several hundred grams it would have been scarcely possible to detect the gallium in the Mount Melville ore. These ores had not been roasted, and in this they differed from the sample received from the North Eastern Steel Works. The effect of roasting is the same as increasing the proportion of gallium in the ore.

Estimation of Gallium in the Blast Furnace Metal from Middlesbrough.

The sample weighing 575 grams consisted of 155 grams of fine powder and 420 grams of coarse powder. The latter portion was heated with hydrochloric acid until the acid was nearly neutralised, when the liquid was decanted and filtered.

Residue A. Solution B.

The *residue A* was heated with hydrochloric acid to which a small quantity of nitric acid was added from time to time; the solution was diluted and filtered.

Residue C. Solution D.

Residue C.—Dried and heated 0.5 gram in the oxyhydrogen flame. The lines of gallium, chromium, nickel, and iron are strong, and lines of sodium, manganese, potassium, copper, and silver are also present.

Solution B.—Boiled for two hours with part of the finely powdered sample added gradually to neutralise all the free acid, so that the gallium in the solution might be precipitated as a basic salt.* The solution was decanted and filtered. The residue was boiled with *solution D*, to which the remainder of the finely powdered sample was slowly added; after boiling for several hours the solution was filtered, and the *residue F* washed with water. The filtrate was mixed with that from *solution B*, the mixture forming *solution G*, which should be free from gallium. This solution was boiled with freshly precipitated copper hydrate,† and the precipitate examined spectrographically for gallium. It contained none.

Residue F.—Boiled with an excess of hydrochloric acid, diluted, filtered, and washed, *Residue H. Filtrate I.*

Residue H.—Dried, powdered, and mixed with *residue C*. Gently heated, the mixture decomposes and expels hydrocarbons, causing the mass to ignite and evolve some white fumes. The substance was thus seen to be very inflammable, and the temperature was reduced as quickly as possible. When cold, it was covered with aqua regia and heated on the water bath for several hours, then diluted and filtered. Filtrate added to *I*, forming *solution K. Residue L.*

Residue L.—A small quantity of it was heated in the oxyhydrogen flame. The gallium line is strong. 45 c.c. of strong sulphuric acid was heated in a porcelain basin until it gave off white fumes; the residue was then added forming a pasty mass which was kept hot for about three hours; white fumes being emitted during the whole time. Water was then added, and the liquid filtered. *Filtrate N. Residue M.* A portion of the latter was heated in the oxyhydrogen flame. The gallium line is still present.

Besides the small quantity remaining in the *residue M*, the gallium should now be in the *solutions K* and *N*. *Solution K* was evaporated nearly to dryness to expel the excess of acid, then diluted, saturated with sulphur dioxide, nearly neutralised with ammonia, and boiled to

* 'Comptes Rendus,' vol. 93, p. 818. See also a complete account, 'Séparation du Gallium d'avec les autres éléments,' par M. Lecoq de Boisbaudran. Paris, Gauthier-Villars. 1884. Reprinted from the 'Annales de Chimie,' 6. Série, t. 2.

† 'Comptes Rendus,' vol. 94, p. 1154.

reduce the iron to the ferrous state. This operation was unsuccessful, a quantity of iron remaining in the ferric state. The *solution N* was, therefore, added and the mixture evaporated that the more volatile acids might be expelled by the sulphuric acid. On adding water to the residue a small quantity of matter remains undissolved; it was removed by filtration. *Residue M₂*.

Up to this stage no reagent had been used which was likely to contain gallium, and we had to consider which of the processes known to separate gallium would be suitable under the conditions of our analysis. The simplest would have been to boil with iron or zinc, but gallium is found associated with both of these metals, and it was decided not to use them. Precipitation by barium carbonate would have been easily effected if sulphuric acid had not been present in such quantity. But, to avoid inaccuracy, the best—although more troublesome process—seemed to be the precipitation of the phosphates of the sesquioxide metals in an acetic acid solution, there being phosphoric acid already in the liquid. The precipitates should contain all the gallium, chromium, and aluminium as phosphates and some phosphate of iron. The gallium is easily separated from chromium and iron by fusion with caustic soda, and from phosphoric acid, aluminium, and chromium by precipitation with potassium ferrocyanide.

The iron was first reduced by passing sulphur dioxide into the solution until it became strongly charged, and heating to boiling, with addition of ammonia, to neutralise the excess of free acid. The addition of ammonia was continued until the white precipitate which formed remained undissolved after boiling for two or three minutes. Boiling water was then added to make the volume of the solution about four litres; this dilution caused a large quantity of light coloured precipitate to form. Ammonium acetate was added, and the liquid, after boiling for several minutes, filtered.

Residue O.—The filtrate was boiled and ammonium carbonate added until a quantity of pale, greenish-coloured precipitate was deposited. More ammonium acetate was added, and the liquid, still acid with acetic acid, was filtered. *Residue P*.

The process just described was repeated with the *filtrate*, the *precipitate R* being slightly darker than *P*. *Filtrate Q*.

Small quantities of the three *residues*, *O*, *P*, *R*, were examined spectrographically. The gallium lines are strongest in *R*. The *filtrate Q* was again boiled with addition of ammonium carbonate to neutralise some of the excess of acid, and the *precipitate S*, small in quantity and of a dark green colour, was removed by filtration. It contained only a trace of gallium.

The *precipitates O* and *S*, containing a much larger proportion of iron than *P* and *R*, were dissolved in hydrochloric acid, and the

gallium, &c., precipitated, after reducing the iron to the ferrous state. *First precipitate, U.* The second contained some gallium; the third, very dark in colour, was free from that metal.

The *precipitates P, R,* and *U* were dissolved in hydrochloric acid, and the solutions filtered to remove a small quantity of insoluble matter which was added to *residue M*. Two drops of violet-coloured filtrate were tested with potassium ferrocyanide, and so marked was the reaction that it was decided to repeat the process of reduction and precipitation to remove as much iron as possible. The first *precipitate W* contained nearly all the gallium; the second contained a small quantity, and the third contained none.

The first and second precipitations *U*, whose spectra are seen in 134¹ and 134³, contain a small quantity of gallium. They were redissolved, reduced, and boiled with excess of ammonium acetate, and the precipitate collected. A second precipitate was free from gallium. The former was fused with caustic soda, extracted with water and filtered. The filtrate was acidified with hydrochloric acid, and boiled with ammonia for some time, and the gallium phosphate thus precipitated was collected. This precipitate was added to *W*.

Residue W, &c.—This contained principally gallium and chromium phosphate with some iron phosphate. It was dissolved in hydrochloric acid, and the solution made to contain about one-fourth its volume of strong hydrochloric acid. Potassium ferrocyanide was added, but not an excess, and the bulky precipitate collected. An excess of the reagent was added to the filtrate, which, after standing twenty-four hours, was filtered. Very small quantities of the two precipitates were examined spectrographically; the second is decidedly richer in gallium than the first.

Residues M and M² with the small Residues added to them as described.—Ignited at a red heat to burn combustible matter. The mass became grey and weighed, when cold, 8 grams. It was very bulky, and consisted largely of silica. Fusion with fusion mixtures converted the silica into alkaline silicates, which were removed by solution in water, leaving a black residue. This was fused with caustic soda and sufficient nitre to oxidise the graphite, &c. Water dissolved all of this, excepting a small quantity of red oxide of iron, part of which was examined for gallium. None present.

The filtrate was acidified with hydrochloric acid, evaporated to dryness, and dried at 120° C. to dehydrate silicic acid.

The dry residue was digested with strong hydrochloric acid, and water added. It was then filtered to remove some silica, which was found to have retained only a trace of gallium.

The filtrate was mixed with a small excess of ammonia, and boiled for some time; the gallium being precipitated probably as phosphate. The filtrate in this and in all similar cases was again boiled, after

adding a few drops of ammonia; if any precipitate was produced it was collected and added to the other precipitate. The precipitate in this case was added to ferrocyanide precipitates obtained from the *residue W*. The paper, after being scraped to remove the residue as far as possible, was burnt in the oxyhydrogen flame. The gallium lines are strong.

The ferrocyanide precipitates with others rich in gallium were ignited at low redness to decompose the cyanides, and then fused with pure caustic soda. The product was extracted with water and filtered.

Residue from Fusion.—Dissolved in hydrochloric acid, expelled the excess of acid, added water, reduced the ferric salt, and filtered. Residue remaining contained only a trace of gallium.

Filtrate.—Boiled with an excess of ammonium acetate and filtered off the precipitate. The filtrate was mixed with sodium phosphate and boiled, thus yielding a second precipitate. The filtrate from this was again boiled, and ammonium carbonate added until a third precipitate was produced. Very small portions of these three precipitates were burnt in the oxyhydrogen flame. The first two were rich in gallium, while the third contained only a trace. Ignited the first and second precipitates, heated the residue in a platinum crucible with hydrochloric and sulphuric acids, expelled the former acid by heating until the white fumes of sulphuric acid were evolved, and then fused the residue with caustic soda. Extracted with water and filtered. After a second fusion the residue was practically free from gallium. The alkaline filtrates were acidified with hydrochloric acid, and the gallium precipitated by boiling with ammonia until the excess of ammonia was expelled. Filtered and tested the filtrate by repeating the process of boiling with ammonia until no further precipitate resulted.

The precipitates of gallium hydrate and phosphate, obtained as described, were dissolved in hydrochloric acid and, after adding one-fourth the volume of the solution of strong hydrochloric acid, an excess of potassium ferrocyanide was added. After standing for one day the precipitate was collected, washed, and ignited. It weighed 0.0670 gram.

This residue was dissolved by heating with strong sulphuric acid in a platinum crucible, some water being added, after heating strongly, and then an excess of caustic soda prepared from sodium. The crucible was then heated until the water was expelled, and the residue retained in the fused caustic soda. The process was repeated on the residue which remained after adding water and filtering. The second residue was practically free from gallium.

The filtrates were collected in a platinum basin, made faintly acid with hydrochloric acid, and saturated with sulphuretted hydrogen.

A brownish coloured precipitate was removed by filtration. It contained copper, lead, and silver, but no gallium. The filtrate was boiled to expel sulphuretted hydrogen, and the gallium precipitated with ammonia as described above. The precipitate was collected and ignited. It weighed 0.0288 gram.

This residue possessed a very light yellow colour. One milligram was burnt in the oxyhydrogen flame; its spectrum shows the two gallium lines very strongly. Lines of sodium, potassium, iron, calcium, and lead are present, but those of the last three are exceedingly weak.

The remaining 0.0278 gram of residue was fused with hydrogen potassium sulphate; water and sulphuric acid were added, and the crucible heated until fumes of sulphuric acid were evolved. Water was again added, and a small residue removed by filtration. This residue weighed 0.0040 gram.

The gallium was separated from the iron by two extractions with caustic soda solution. The ferric hydrate was dissolved in hydrochloric acid, and reprecipitated by ammonia. The ferric oxide weighed 0.0022 gram.

The gallium in the filtrate was then reprecipitated and weighed as oxide. It weighed 0.0213 gram.

A few drops of sodium phosphate were added to the filtrate, and sufficient ammonia to make it turn red litmus paper blue. After boiling for a few minutes the liquid was filtered, the paper being dried and burnt in the oxyhydrogen flame. The gallium lines are present in its spectrum, but are very weak.

The oxide of gallium now possessed a scarcely perceptible, faint yellow colour. It does not represent the whole of the gallium present in the sample, as a small quantity was removed and lost in testing the precipitations and residues. We are able, however, to estimate this quantity by comparing the lines in the different spectra with lines and spectra obtained by heating weighed quantities of gallium oxide. In this way we estimate the total quantity of gallium to be as follows:—

	Ga ₂ O ₃ .
Pure oxide	0.0213 gram.
In 0.001 gram of impure oxide....	0.0008 „
In residue insoluble in HKSO ₄	0.0004 „
In other substances.....	0.001 „

Ga₂O₃, total 0.0235 gram.

0.0235 gram of pure Ga₂O₃ contains 0.0175 gram of gallium,

$$\text{equal to } \frac{0.0175 \times 100}{575} = 0.00304 \text{ per cent.}$$

One part of gallium is contained in 33,000 parts of crude iron.

An estimation of the gallium in the "mixer metal" had been attempted in the spring of this year, but the separation was not as complete as in the process just described. The figure obtained, however, is so closely in accord with the above that we will briefly describe the process and record the result.

The sample, weighing 340 grams, was boiled with hydrochloric acid until the latter was nearly neutralised; the solution was then decanted, and fresh acid added to the residue. When the acid ceased to have any marked action the whole liquid was filtered, and the *residue A* washed, dried, and treated separately for the separation of gallium.

Filtrate B.—From this filtrate gallium was precipitated by calcium carbonate, but phosphates and sesquioxide metals, including chromium, rendered the precipitate a too complex mixture, and we had recourse to the ferrocyanide method.

The gallium was separated from the iron by pure sodium hydrate, and finally precipitated as hydrate and ignited. The oxide weighed 0.0149 gram, and this amount corresponds to 0.0033 per cent. of gallium in the sample or one part in 30,000 of the iron.

We know, by the spectrographic examination of the residues, &c., that the whole of the gallium was not obtained, and that the oxide weighed was not quite pure gallium oxide, but with the experience gained in this estimation we were able to make the more exact analysis already described.

In conclusion, we may state that this blast furnace metal contains more gallium than the richest source of that element hitherto known. The mineral referred to is a zinc blende from Bensburg on the Rhine, about eight miles from Cologne; it is found in the Franzisca adit of the Lüderich mine. MM. Lecocq de Boisbaudran and Jungfleisch extracted 62 grams of crude gallium from 4300 kilograms, or nearly $4\frac{1}{4}$ tons of the ore; this is in the proportion of 1 in 72,000, but they believed the actual quantity present to be about 1 part of gallium in 50,000 of the ore.

We have recently discovered other sources of gallium, but cannot include the details of our later work in the present communication.